

10/549600

A06955

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
17 June 2004 (17.06.2004)

PCT

(10) International Publication Number
WO 2004/050759 A1

(51) International Patent Classification⁷: C08L 29/14

(21) International Application Number:
PCT/US2003/038099

(22) International Filing Date:
26 November 2003 (26.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/429,456 27 November 2002 (27.11.2002) US
UNKNOWN 25 November 2003 (25.11.2003) US

(71) Applicant (*for all designated States except US*): E. I. DU
PONT DE NEMOURS AND COMPANY [US/US]; 1007
Market Street, Wilmington, DE 19898 (US).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): HOFMANN, George,
Henry [US/US]; 102 Weldin Park Drive, Wilmington, DE
19803 (US).

(74) Agent: DOBSON, Kevin, S.; E.I. DUPONT DE
NEMOURS AND COMPANY, LEGAL PATENT
RECORDS CENTER, 4417 Lancaster Pike, WILMING-
TON, DE 19805 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: THERMOPLASTIC ELASTOMERS FROM CROSSLINKED POLYVINYLBUTYRAL

(57) Abstract: The present invention is a thermoplastic elastomer (TPE) composition comprising crosslinked elastomeric PVB and a thermoplastic polymer, and a process for making said TPE composition.

WO 2004/050759 A1

THIS PAGE BLANK (USPTO)

THERMOPLASTIC ELASTOMERS FROM CROSSLINKED POLYVINYL BUTYRAL

5

BACKGROUND OF THE INVENTION

Field of the Invention

10 This invention relates to thermoplastic elastomers comprising polyvinylbutyral.

Description of the Related Art

Polyvinyl butyral (PVB) is a thermoplastic material useful for imparting shatter-resistance to glass in such applications as windshields
15 for automobiles and window glass in homes and buildings, for example. The preparation of polyvinyl butyral is known, and is practiced commercially. For example, Butacite® is a polyvinyl butyral product manufactured by E. I. DuPont de Nemours and Company. Solutia also manufactures polyvinyl butyral products.

20 It is known that PVB blends with other polymer materials have utility. For example, U.S. Patent No. 5,514,752 describes PVB/polypropylene blends, and U.S. Patent No. 5,770,654 describes PVB/polyamide blends. U.S. Pat. No. 6,506,835 describes PVB/PVC blends. PVB can improve the flexibility, polarity and toughness of
25 polyolefins, polyamides, and polyvinylchloride. However, use of PVB in polymer blends is not without problems.

PVB is a material that can be difficult to work with because of the tendency of PVB to adhere to itself. Sheets of PVB can stick together, or bind, with such strength that it is very difficult to separate the layers - even
30 to the extent that the layers cannot be separated. Such irreversible self-adhesion by PVB is referred to in the art of PVB manufacture as "blocking". Once PVB "blocks", it can be extremely difficult, if not impossible, to process. PVB is generally stored cold to reduce the

tendency to block. Refrigerated vehicles are used to ship PVB for the same reason. The tendency to block can make manufacturing processes that incorporate PVB very complex and difficult. Continuous processes that in which PVB is handled can be very expensive processes to run, and therefore are not practical commercial operations. Blends of PVB with other materials can block in the same manner as homogenous PVB compositions. Therefore, blends of PVB with other polymers can be difficult to obtain in a cost effective manner.

Thermoplastic elastomers (TPEs) are composite materials obtained from the combination of an elastomeric material and a thermoplastic material. TPEs are elastomeric materials that are dispersed and crosslinked in a continuous phase of a thermoplastic material. Examples of conventional TPEs include Santoprene®, available from Advanced Elastomers Systems, Inc. and Sarlink® available from DSM Elastomers, Inc.

TPEs are useful in many applications, including hose, tubing, liners, seals, sheeting belts, wire and cable jackets, wheels, and grips, for example. To date there are no TPEs which include PVB.

SUMMARY OF THE INVENTION

The present invention is a thermoplastic elastomer (TPE) composition comprising crosslinked polyvinylbutyral (PVBX) and a thermoplastic polymer, wherein the thermoplastic polymer is a continuous phase of the TPE having dispersed therein the elastomeric PVBX.

In another aspect, the present invention is a process for preparing a composition comprising a PVBX elastomer dispersed in a thermoplastic polymer continuous phase comprising the step of using a crosslinking agent to crosslink a modified non-blocking PVB composition in the presence of a thermoplastic polymer to form PVBX as a dispersed elastomer in the thermoplastic polymer phase.

TPE blends that incorporate PVB can be desirable because PVB can increase adhesion, reduce color, and increase the polarity -- therefore the oil resistance

-- of the TPEs of the present invention compared with conventional TPEs.

5

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, the present invention is a TPE comprising an elastomer that is a crosslinked polyvinyl butyral (PVBX) that is obtained from a modified non-blocking polyvinylbutyral (PVB) composition.

Unmodified PVB is an uncrosslinked gum that flows and masses together, that is it blocks, typically at temperatures above about 4°C (approximately 40°F). For this reason it is difficult to convert PVB into a blended material, particularly by a continuous process. Modified PVB useful in the practice of the present invention is free-flowing, without blocking (non-blocking) at temperatures above about 4°C. Suitable modified PVB compositions are described in U.S. Provisional Patent Application Ser. No. 60/224126, the teachings of which are incorporated herein by reference in its entirety.

Modified PVB suitable for use in the practice of the present invention can be obtained commercially. For example, modified PVB can be purchased under the tradename of ECOCITE™ from E. I. DuPont de Nemours and Company (DuPont). Suitable modifying agents for the purposes of the present invention include, for example, Fusabond P MD-353D, Fusabond A MG-423D, and Fusabond E MB-496D, available from DuPont.

Modified PVB can be crosslinked using any crosslinking agent that is capable of reacting with the hydroxyl groups of PVB. A crosslinking agent suitable for use herein is any polyfunctional molecule wherein the crosslinking agent's functional groups are the type that can react with the hydroxyl groups of PVB to form a crosslinked network of PVB polymer molecules. Suitable crosslinking agents include poly-carboxylic acids such as a di-, tri-, and tetracarboxylic acids, for example and/or functional equivalents thereof. Functional equivalents of carboxylic acids for the

purposes of the present invention include, for example, carboxylic acid esters, carboxylic acid anhydrides and mixed anhydrides, carboxylic acid halides, alkyl sulfonates, and lactones, for example. Crosslinking agents having mixed functionality may be suitable for use herein. Other suitable crosslinking agents may be known by one skilled in the art to be useful herein, and use of that agent in the present invention is not excluded because it is not listed herein. Suitable crosslinking agents include, for example: adipic acid; succinic acid; maleic acid; citric acid; ethylenediamine tetraacetic acid (EDTA); succinic anhydride; maleic anhydride; phthalic anhydride; trimellitic anhydride; pyromellitic dianhydride (PMDA); benzophenone tetracarboxylic acid dianhydride (BTDA); poly(methyl vinyl ether, comaleic anhydride); and poly(styrene, comaleic anhydride); isomers of terephthalic acid; and succinic acid half-methyl ester; 4,4'-methylene diphenyl diisocyanate (MDI); 2,4-toluene diisocyanate (TDI); diisocyanate oligomers such as, for example, TDI-terminated poly(propylene glycol), TDI-terminated poly(ethylene adipate), TDI-terminated poly(1,4-butanediol), and/or TDI-terminated poly(ethylene glycol); naphthalene diisocyanate (NDI); hexamethylene diisocyanate (HDI); p-phenylene diisocyanate (PPDI). Suitable crosslinking agents can also include, for example: diepoxides such as: glycerol diglycidyl ether; neopentylglycol glycidyl ether; bisphenol A diglycidyl ether; poly(propylene glycol) diglycidyl ether; ethylene glycol glycidyl ether; 1,4-butanediol diglycidyl ether; and, polyethylene glycol diglycidyl ether. Suitable crosslinking agents can also include, for example: silanes such as 3-aminopropyl triethoxysilane, vinyl triethoxysilane; vinyltrimethoxy silane. Suitable crosslinking agents can also include, for example: phenolics such as octyl phenol-formaldehyde resin; dimethylol phenolic resin. Suitable crosslinking agents can also include, for example: melamine resins.

PVBX is an elastomer that can be formed after reacting PVB or modified PVB with a crosslinking agent. Conventional PVB can be difficult to use in polymeric blends, and so use of modified PVB is preferred in the practice of the present invention.

PVBX can be included in the TPE in an amount of from about 1 wt% to about 99 wt% of the total weight of the TPE. Preferably the PVBX is included in an amount of from about 25 wt% to about 95 wt%, more preferably in an amount of from about 50 wt% to about 90 wt%, and most preferably in an amount of from about 75 wt% to about 90 wt%.

The thermoplastic polymer can be any that forms a discrete phase, but shows functional compatibility, with PVB or modified PVB. For example, the thermoplastic polymer can be a polyolefin such as polypropylene or polyethylene, including high density polyethylene (HDPE); polyvinylchloride; polyamides; polycarbonate; polyacrylic acid; polyacrylate; polymethyl methacrylate; polystyrene; styrenic copolymers; polyvinylidene chloride; polyesters; polyacetals; copolyesters; and, polysulfones. The thermoplastic polymer can be included in an amount of from about 99 wt% to about 1 wt%, preferably in an amount of from about 75 wt% to about 5 wt%, more preferably from about 50 wt% to about 10 wt%, and most preferably from about 25 wt% to about 10 wt%.

In another embodiment, the present invention is a process for preparing a TPE comprising PVBX and a thermoplastic polymer. In the present invention, modified PVB is crosslinked to form the PVBX elastomer of the present invention. The modified PVB can either be formed from the reaction of PVB and a modifying agent, or modified PVB can be purchased commercially. The preparation of modified PVB is described in detail in U.S. Provisional Patent Application Ser. No. 60/224126. To prepare modified PVB, for example, PVB can be heated in the presence of a modifying agent which has hydroxyl-reactive groups such as the anhydride functionality of Fusabond® P, obtained commercially from E. I. DuPont de Nemours and Company, for example.

A catalyst can be optional for the crosslinking reaction, depending on the nature of the crosslinking agent. It is preferred that a catalyst be used to facilitate the crosslinking reaction. One skilled in the art will know what catalyst is suitable, depending on the identity and functionality of the crosslinking agent. For example, conventional catalysts for esterification

reactions can be used if the crosslinking agent is a polycarboxylic acid, or conventional transesterification catalysts can be used if the crosslinking agent is an ester. Divalent tin catalysts, for example, are suitable for use herein. For example, stannous octanoate, stannous acetate, and
5 stannous chloride can be useful catalysts for the purposes described herein. Conversely, peroxide catalysts are not useful in the practice of the present invention. The amount of catalyst added can also be dependent upon the nature of the reactants. One skilled in the art will know that the more catalyst added, the faster the reaction will take place generally. It is
10 within the skill of one of ordinary skill in the art to determine the appropriate levels of catalyst required for the particular crosslinking reaction.

Other optional components can be added such as antioxidants, pigments, dyes, fillers, plasticizers and the like. For example, fillers such
15 as carbon black, talc, calcium carbonate, and clays can be suitable for use herein. Plasticizers such as diisononylphthalate (DINP), di-2-ethylhexyl azelate, adipic acid polyesters, azelaic acid polyesters, tri-2-ethylhexyl trimellitate are also suitable for use herein. Antioxidants suitable for use herein include, Irganox 1010 available from Ciba Specialty Chemicals, Inc.
20 and Ethanox 702 available from Albemarle Corp.

Preferably, TPEs of the present invention will have a tensile strength (max) of greater than 800 psi, and an elongation of greater than 200%.

EXAMPLES

25 The Examples and Comparative Examples are presented for illustrative purposes only, and are not intended to limit the scope of the present invention in any manner.

In the Examples, for each blend the components, with the exception of a crosslinking agent, were blended in a Haake/Brabender mixer at
30 200°C @ 100 to 150 rpm in the proportions indicated in Table 1, until the mixture becomes homogeneous. The temperature was then increased to 230°C and the crosslinking agent was added to the blend, and mixing

continued for 2 minutes after the torque levels out. Each blend was removed from the blender and quickly pressed flat and quenched in dry ice, and then dried in a vacuum oven at room temperature. The Comparative Example did not include adipic acid.

5

Table 1

Component	Wt. % in Ex. 1 ^a	Wt. % in Ex. 2	Wt. % in Ex. 3	Wt. % in Ex. 4
Polypropylene ¹	13.9	13.7	13.6	13.4
PVB	83.2	82.1	81.5	80.4
Fusabond P ²	2.8	2.7	2.7	2.7
Stannous acetate	0	0.7	0.7	0.7
Adipic acid	0	0.7	1.4	2.7
Irganox® 1010	0.1	0.1	0.1	0.1

¹Profax 6323²MD-353D

^aComparative Example, not an example of the present invention. The blends were tested, and the results are given in Table 2.

10

Table 2

Property	Ex. 1	Ex. 2	Ex. 3	Ex. 4
MI ¹ @190°C, 2160 g	4.8	0.6	0.2	0.0
MI ¹ @190°C, 21.6 kg	-	-	67	14
Tensile Strength Max (PSI)	3817	3106	3315	869
Elongation @ MAX (%)	285	243	243	89
Shore A (0/15 sec)	77/68	81/72	85/74	82/68
Shore D (0/15 sec)	54/23	53/22	54/25	53/22
Compression Set ² (%)	48/113	46/113	42/106	32/75

¹MI = melt index²@ 23°C & 100°C

15

The blends described in Table 3 were prepared as described for the Examples in Table 1, except that all ingredients except for DINP were blended at 180°C until homogeneous, then DINP was added and blended for 1 minute. Samples were removed, pressed flat, quenched in dry ice, then dried in a vacuum oven at room temperature.

20

The peroxide crosslinking agent of Table 3 is ineffective in crosslinking PVB, as evidenced by the lack of significant reduction in melt indices and compression sets.

Table 3

Component	Wt. % in Ex. 5 ^a	Wt. % in Ex. 6 ^a	Wt. % in Ex. 7 ^a	Wt. % in Ex. 8 ^a
Polyvinyl chloride ¹	16.1	16.1	16.0	15.9
PVB	64.5	64.3	64.1	63.7
Fusabond MG 423D	3.2	3.2	3.2	3.2
DINP	16.1	16.1	16.0	15.9
Luperco 231XL	0	0.32	0.64	1.27

¹E80428-68^aComparative Example, not an example of the present invention.

5

The blends were tested, and the results are given in Table 4.

Table 4

Property	Ex. 5 ^a	Ex. 6 ^a	Ex. 7 ^a	Ex. 8 ^a
MI ¹ @190°C, 2160 g	0.7	1.3	1.4	3.5
MI ¹ @190°C, 21.6 kg	192	207	192	295
Tensile Strength Max (PSI)	2584	2405	2534	2323
Elongation @ MAX (%)	342	339	346	346
Shore A (0/15 sec)	82/68	80/64	78/63	76/60
Shore D (0/15 sec)	51/20	45/17	50/18	45/16
Compression Set ² (%)	49/96	49/101	44/111	47/106

¹MI = melt index²@ 23°C & 100°C^aComparative Example, not an example of the present invention.

10

The crosslinking agents of Table 5 were effective crosslinking agents as evidenced by the reduction of melt indices and compression sets versus the comparative Example 8, in Table 6.

15

Table 5

Ex. No.	PP ¹	Mod G ²	MDI ³	TDI ⁴	PEA (TDI) ⁵	BTDA ⁶	EGDE ⁷	A-1100 Silane ⁸	R-7500 ⁹
8	50	50	0	0	0	0	0	0	0
9	49.5	49.5	1.0	0	0	0	0	0	0
10	46.5	46.5	0	7.0	0	0	0	0	0
11	41.7	41.7	0	0	16.7	0	0	0	0
12	49.5	49.5	0	0	0	1	0	0	0
12A	47.6	47.6	0	0	0	4.8	0	0	0
13	43.5	43.5	0	0	0	0	13.0	0	0
14	45.5	45.5	0	0	0	0	0	9.0	0
15	41.7	41.7	0	0	0	0	0	0	16.6

¹ Profax 6323; ² See Table 6; ³ 4,4' methylene bis (phenyl isocyanate); ⁴ 2,4 toluene diisocyanate;⁵ poly(ethylene adipate) TDI terminated; ⁶ benzophenone tetra carboxylic dianhydride;⁷ ethylene glycol diglycidyl ether; ⁸ 3-aminopropyl triethoxy silane; ⁹ octyl-phenol formaldehyde resin

Table 6

Ex. No.	Melt Index ¹	Melt Index ²	Shore D	Compression Set @ 70°C
8	6	124	58	93
9	0	10	62	82
10	0	16	67	81
11	0	18	50	81
12	0	19	63	80
12A	0	11	65	83
13	0	30	49	93
14	0	22	64	90
15	0	48	63	90

¹ @ 190 °C, 2160 g² @ 190 °C, 10 kg

WHAT IS CLAIMED IS:

1. A thermoplastic elastomer (TPE) composition comprising crosslinked polyvinylbutyral (PVBX) and a thermoplastic polymer, wherein
5 the thermoplastic polymer is a continuous phase of the TPE having dispersed therein the elastomeric PVBX.
2. The composition of Claim 1 wherein the PVBX is present in an amount of from about 25 wt% to about 95 wt%.
- 10 3. The composition of Claim 2 wherein the PVBX is present in an amount of from about 50 wt% to about 90 wt%.
4. The composition of Claim 3 wherein the PVBX is present in an
15 amount of from about 75 wt% to about 90 wt%.
5. The composition of Claim 1 wherein PVBX is the product of the crosslinking reaction between modified PVB and crosslinking agents
20 selected from the group consisting of: polycarboxylic acids or functional equivalents thereof; diisocyanates; and diisocyanate oligomers.
6. The composition of Claim 1 wherein the continuous phase is at least one thermoplastic polymer selected from polymers in the group
25 consisting of: polypropylenes; polyethylenes; polyvinylchlorides; polystyrenes; polyamides; polycarbonates; poly(acrylic acid); polyacrylates; poly(methy methacrylates); styrenic copolymers; polyvinylidene chlorides; polyesters; polyacetals; copolyesters; and polysulfones.
- 30 7. The composition of Claim 6 wherein the continuous phase is polypropylene or polyvinylchloride.

8. The composition Claim 7 wherein the continuous phase is polypropylene.
- 5 9. The composition of Claim 1 wherein the thermoplastic polymer is present in an amount of from about 75 wt% to about 5 wt%.
10. The composition of Claim 9 wherein the thermoplastic polymer is present in an amount of from about 50 wt% to about 10 wt%.
- 10 11. The composition of Claim 10 wherein the thermoplastic polymer is present in an amount of from about 25 wt% to about 10 wt%.
12. A process for preparing a composition comprising a PVBX
15 elastomer dispersed in a thermoplastic polymer continuous phase comprising the step of using a crosslinking agent in a crosslinking reaction to crosslink a modified non-blocking PVB composition in the presence of a thermoplastic polymer to form PVBX as a dispersed elastomer in the thermoplastic polymer phase.
- 20 13. The process of Claim 12 wherein the crosslinking agent is an agent selected from the group consisting of: polycarboxylic acids or functional equivalents thereof; diisocyanates; and diisocyanate oligomers.
- 25 14. The process of Claim 13 wherein a catalyst is used to catalyze the crosslinking reaction.
15. A process for preparing a composition comprising a PVBX
30 elastomer dispersed in a thermoplastic polymer continuous phase comprising the steps of: (1) combining PVB, a thermoplastic polymer, and a PVB modifying agent; (2) modifying PVB in the presence of the thermoplastic polymer to form a modified non-blocking PVB/thermoplastic

polymer mixture and (3) using a crosslinking agent to crosslink the modified non-blocking PVB/thermoplastic polymer composition to form PVBX as a dispersed elastomer in the thermoplastic polymer phase.

- 5 16. An elastomeric crosslinked polyvinylbutyral composition (PVBX) obtained by a process comprising the steps: (1) heating PVB in the presence of a modifying agent to obtain a non-blocking PVB composition (2) heating the modified PVB composition in the presence of a PVB crosslinking agent and a catalyst, wherein the conditions are sufficient for
10 a crosslinking reaction to take place between PVB and the crosslinking agent, to obtain the elastomeric PVBX.
17. An article prepared from the TPE composition of Claim 1.
- 15 18. The article of Claim 17 wherein the article is a hose, tube liner, seal, sheet, belt, wire and cable jacket, wheel, shoe sole, film, or grip.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/38099

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L29/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C09D C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95/07940 A (MONSANTO CO ; HOPFE HAROLD HERBERT (US); KARAGIANNIS ARISTOTELIS (US)) 23 March 1995 (1995-03-23) page 3, line 18 - page 4, line 12 claims 1,3,6,8	1-6, 9-14,17, 18
X	EP 0 360 420 A (MINNESOTA MINING & MFG) 28 March 1990 (1990-03-28) page 3, line 18 - page 4, line 39 page 7, line 9 - page 9, line 2	1-6, 9-14,17, 18
A	WO 02/12356 A (DU PONT ; HOFMANN GEORGE HENRY (US)) 14 February 2002 (2002-02-14) cited in the application the whole document	1-18

-/--

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 April 2004

Date of mailing of the international search report

28/04/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rodriguez, L

INTERNATIONAL SEARCH REPORT

Inte al Application No
PCT/US 03/38099

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/79305 A (CLARIANT GMBH ; PAPENFUHS BERND (DE)) 25 October 2001 (2001-10-25) claims 1,2 -----	1-18

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/US 03/38099

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9507940	A	23-03-1995	BR 9307887 A	06-08-1996
			WO 9507940 A1	23-03-1995
			AU 681354 B2	28-08-1997
			AU 5131993 A	03-04-1995
			CN 1102840 A ,B	24-05-1995
			CZ 9600681 A3	17-07-1996
			DE 69327174 D1	05-01-2000
			DE 69327174 T2	29-06-2000
			EP 0719288 A1	03-07-1996
			JP 9502755 T	18-03-1997
			JP 3305721 B2	24-07-2002
			KR 180477 B1	15-05-1999
			SK 31696 A3	05-03-1997
			US 5595818 A	21-01-1997
EP 0360420	A	28-03-1990	US 5008142 A	16-04-1991
			AT 136124 T	15-04-1996
			AU 619878 B2	06-02-1992
			AU 3923489 A	08-03-1990
			CA 1336300 C	11-07-1995
			DE 68926081 D1	02-05-1996
			DE 68926081 T2	28-11-1996
			EP 0360420 A2	28-03-1990
			IE 73485 B1	04-06-1997
			JP 3250615 B2	28-01-2002
			JP 11288231 A	19-10-1999
			JP 2113078 A	25-04-1990
			JP 3038218 B2	08-05-2000
			KR 145078 B1	15-07-1998
			US 5256721 A	26-10-1993
			US 5262225 A	16-11-1993
			ZA 8905913 A	30-05-1990
WO 0212356	A	14-02-2002	AU 8332501 A	18-02-2002
			CA 2412461 A1	14-02-2002
			EP 1311562 A2	21-05-2003
			JP 2004506072 T	26-02-2004
			WO 0212356 A2	14-02-2002
WO 0179305	A	25-10-2001	DE 10018517 A1	18-10-2001
			CN 1464884 T	31-12-2003
			CZ 20023398 A3	12-02-2003
			WO 0179305 A2	25-10-2001
			EP 1272534 A2	08-01-2003
			JP 2003531226 T	21-10-2003
			US 2003166788 A1	04-09-2003

THIS PAGE BLANK (USPTO)